
CHAPTER 1

Introduction and Literature Review

1.1 Introduction

Nobel Laureate Richard Feynman earlier presented the specific concept of nanotechnology in his famous speech to the American Physical Society's annual conference in 1959. Since then, scientists have been researching the function of nanotechnology in all aspects of society. The ability to regulate material properties by constructing materials at the nanoscale is what makes nanotechnology so fascinating. Nanotechnology's tunable material properties were originally stated in Norio Taniguchi's article in 1974, when the term "nanotechnology" was first used in a scientific journal [Taniguchi *et al.* (1974)]. Based on a report published by the National Nanotechnology Initiative, the term nanotechnology also became prevalent for the manipulation of matter at the macromolecular, molecular, and atomic scales that is also particularly appropriate for meticulous structures, and device systems. Nanotechnology has attracted the attention of the science community over the past several decades in various fields including chemistry, physics, biotechnology and electronics [Offenhäusser *et al.* (2009), Roco *et al.* (2007), Zhu *et al.* (2004)]. Due to their potential applications and properties towards diverse sectors like as catalysis, pesticides, stain resistant clothing, sunscreens, automotive paints, light emitters, digital cameras, single electron transistors, biomedical, electronics, health care, space industries, drug-gene delivery, mechanics, optics, agriculture, diagnosis, chemical industries, science, environment and energy [Murty *et al.* (2013), Mangaraj *et al.* (2020), Clayton *et al.* (2018)].

Nanomaterial are one of the ultimate components of nanotechnology. Nanomaterial are particles between 1 and 100 nanometers in size, composed of carbon, metals, metal oxides or organic materials [Ealia *et al.* (2017), Haruta *et al.* (2002), Aitken *et al.* (2006)]. Nanomaterial demonstrated exceptional chemical, biological and physical properties at the Nano scale compared to associated particles on a wider scale. Above discussed phenomenon can be attributed to increase in reactivity or stability in chemical process,

larger surface area, and increase in mechanical strength in addition to quantity. These properties can be used for its various applications [Kumar *et al.* (2009), Ealia *et al.* (2017), Mageswari *et al.* (2016), Baig *et al.* (2021)].

In addition to their structure, nanomaterials have a variability of dimensions (0D, 1D, 2D, 3D), shapes (spherical, cylindrical, tubular, conical, hollow core) and sizes (1-100 nm) [Thakur *et al.* (2022), Xia *et al.* (2003)]. At the point where length, width and height can be fixed simultaneously, a nanomaterial can be zero dimensional for instance fullerenes, nano dots, one dimensional, where only one parameter such as length or width or height e.g. graphene, two dimensional having only two parameters with length and width e.g. carbon nanotubes and three dimensional having such three parameters like length, width and height like gold nanoparticles, diamond which is cultured in all dimensions. The various kinds of nanomaterials that exist are inorganic nanomaterial, organic nanomaterial, and carbon nanomaterial [Georgakilas *et al.* (2015), Tiwari *et al.* (2012), Ferrari *et al.* (2015)].

Till now, several scientific researchers have manufactured metal and metal-oxide inorganic-based nanomaterials [Vallet-Regí *et al.* (2019), Wang *et al.* (2020)]. Inorganic metal based nanomaterials usually involve silver, gold, aluminium, cadmium, copper, iron, zinc, and lead nanomaterials, whereas metal oxide-based inorganic nanomaterials incorporate zinc oxide, copper oxide, titanium dioxide, cerium oxide, as well as iron oxide [Ealia *et al.* (2017), Majhi *et al.* (2021)]. These materials are important in our communities and also employed in electronics, photonics, water splitting, chemical sensors, biosensors, diagnosis, and water treatment applications [Tyagi *et al.* (2020), Bhalla *et al.* (2020), Huang *et al.* (2011) Ghosh *et al.* (2015)].

Biomolecules such as nucleic acids, peptides, or proteins, as well as organic building blocks like small molecular drugs, fluorescent dyes, and π -conjugated semiconductor materials, have been widely used to construct attractive Nano-architectures with different topologies and dimensions. Organic nanoparticles or polymers are usually recognized as dendrimers, micelles, liposomes, and ferritin, and many others. Various nanomaterials, such as micelles and liposomes, have a hollow core, usually known as nanocapsules, and therefore are sensitive to temperature and electromagnetic fields such as light and heat [Pu *et al.* (2011), Chen *et al.* (2020), Sahu *et al.* (2021), Sulthana *et al.* (2021) Khalid *et al.* (2020)].

Organic nanomaterials have a wide range of applications in the field of drug delivery, bio imaging, and disease diagnosis, as well as unique properties such as tuneable synthesis, ease of fabrication, excellent biocompatibility, and low cytotoxicity [Liang *et al.* (2014), Broza *et al.* (2014) Zhang *et al.* (2021)].

Carbon based nanomaterial is now the key focus, which has resulted in substantial progress in nanoscience [Cha *et al.* (2013)]. Carbon is one of the most abundant and versatile elements in the biosphere and member of the carbon family [Sharma *et al.* (2017), Su *et al.* (2013)]. It can form allotropes, which also have physical and chemical characteristics influenced by the structural geometry of atoms and chemical binding between molecules. This intriguing feature enables carbon to build a variety of structures with varying outstanding characteristics. Carbon is being used to produce carbon based nanomaterials like as graphite, graphene, carbon nanotubes, graphene oxide, nanodiamonds, fullerenes, graphene quantum dots and carbon quantum dots as shown in **Fig 1.1** [Serrano-Aroca *et al.* (2021)], and they exhibit unique qualities such as great mechanical strength and conductivity, as well as attractive optical properties and chemical adaptability. These nanoparticles are also beneficial for commercial applications because of the abundance of raw ingredients for large-scale manufacture and successful synthetic approaches. This

intriguing property enables carbon to build a wide range of structures with differing essential features. The abundance of raw components for large-scale manufacturing and excellent synthetic procedures, these nanomaterials are also useful for several applications such as catalysis, bioimaging, biosensing, drug delivery, electronics, and photodynamic therapy. Carbon-based nanomaterials have a number of distinguishing characteristics, including inherent fluorescence, a tuneable narrow emission spectrum, strong photostability, low cytotoxicity, and a large surface area. The fundamental core structure and surface chemical moieties of all of these nanomaterials have been identified to be distinctive. The highly fluorescent carbon dots are a recent addition to the carbon based nanomaterial family.

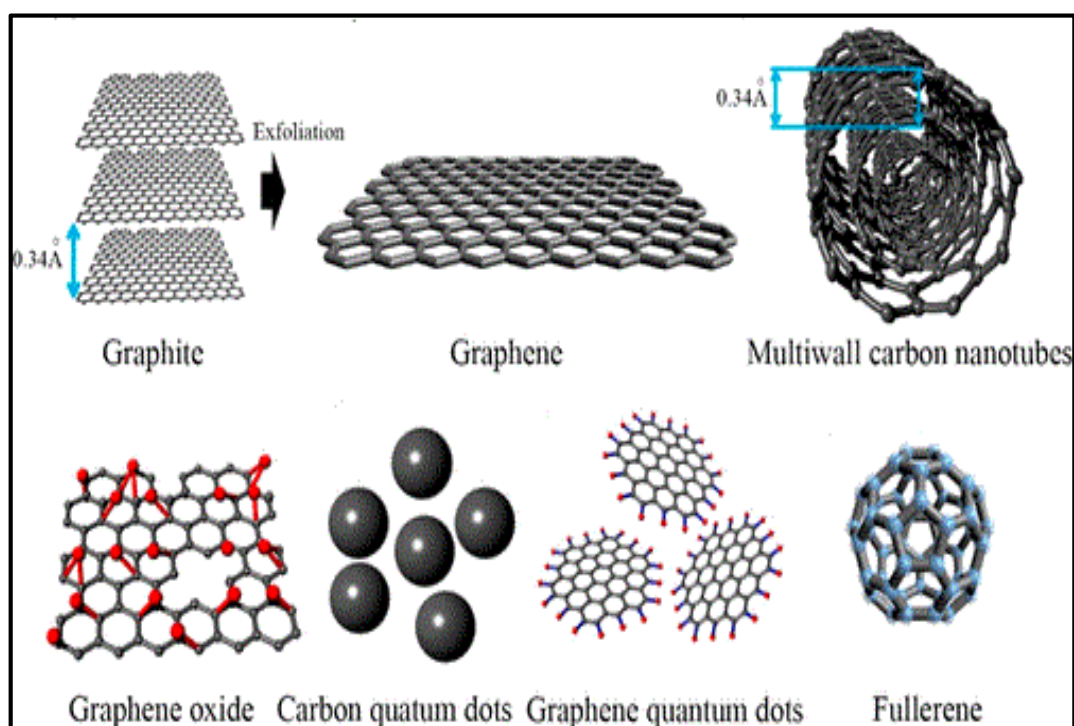


Figure 1.1 Structure of few carbon-based nanomaterials.

1.2 Carbon quantum dots

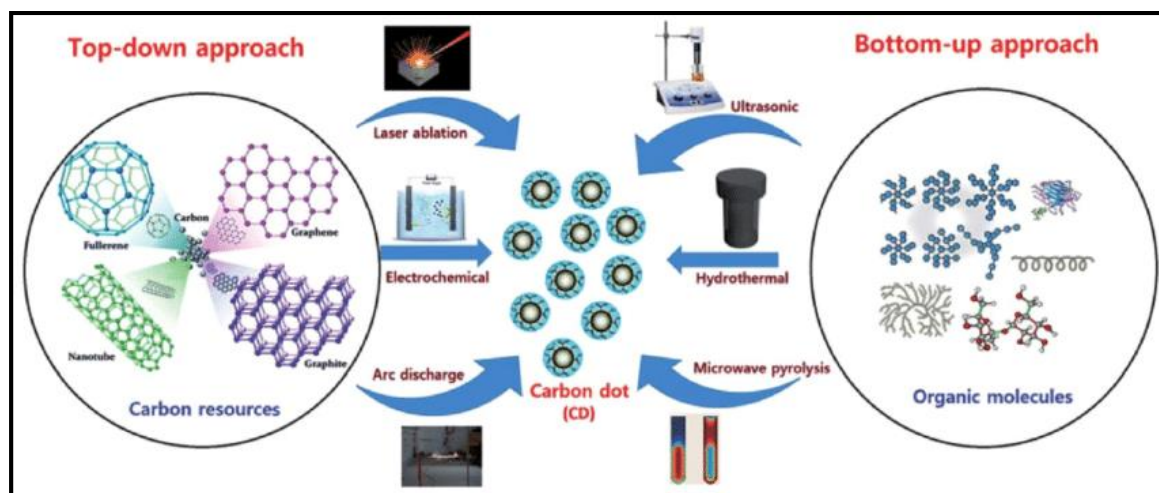
Carbon quantum dots are a zero-dimensional carbon-based fluorescent nanomaterial that has been gradually rising in popularity in the scientific community. Their remarkable tuneable emission, non-toxicity, and environmentally compatible properties have recently piqued research. In 2004, Xu et al. found carbon quantum dots with less than 10 nm in size, while trying to manufacture single walled carbon nanotubes. Experiments with single-walled carbon nanotubes resulted in the discovery of CQDs by coincidence. Since then, the fluorescence properties of CQDs have been extensively researched, and they have evolved into a whole new class of biocompatible fluorescent nanomaterials. These small carbonaceous compounds were given the scientific name CQDs in 2006 by researchers working on surface passivation to enhance fluorescence. In contrast to CQDs, the fabrication of semiconductor quantum dots, which is often constructed of heavy metals, seems to have significant limits in terms of their broad range of applications. Because heavy metals are extremely harmful even in small doses, clinical experiments are not permitted to utilise them. Although the Weller research group gave the idea of synthesising biocompatible semiconductor quantum dots in aqueous phase from CdClO_4 , it challenges a lot of barriers, poor quantum yield and a large surface area distribution. Several scientists have synthesised metal based semiconductor quantum dots like as Peng *et al.* prepared and characterized CdS, CdSe and CdTe semiconductor quantum dots by using these precursors including cadmium acetate, 3,3-thiodipropionic acid, and hydroxyl propyl acrylate and trioctylphosphine oxide [Peng *et al.* (2001)]. To synthesize CdS-sulphydryl semiconductor quantum dots, Vossmeier *et al.* used $\text{Cd}(\text{ClO}_4) \cdot 6\text{H}_2\text{O}$, H_2S , and thioglycerol as precursors in aqueous solution along with thioglycolic acid [Vossmeier *et al.* (1994)]. Aqueous-soluble CdS quantum dots for silver-ion sensing were synthesised by Song Han *et al.* [Wang *et al.* (2021)]. However, in terms of biological applications, it still has a number of

limitations. Surface morphology and functionalization of semiconductor quantum dots have indeed become the most critical parameters in adapting them for biomedical application. However, surface modification often does not produce good results; in most cases, it faces significant challenges such as poor luminescence, chemical disintegration, photo-etching, and potential toxicity due to Cadmium ion leaching, and in other cases, quantum dots lost their fundamental properties [Kershaw *et al.* (1999)]. Due to the limitations of semiconductor quantum dots, CQDs were developed to replace them. They have a minimal side effects, excellent biocompatibility, cost effective, good water solubility, and bright fluorescence [Cao *et al.* (2007)]. Carbon quantum dots are a new type of luminescent nanomaterial which is free of heavy metals and have generated a lot of excitement in recent years. It has a carbon core or intrinsic core with sp^2 and sp^3 hybridisation state, as well as a shell containing carboxylic, hydroxyl, carbonyl, amine, and other functional groups [Shamsipur *et al.* (2018)]. Besides giving excellent water solubility, high quantum yield, and chemical stability, these functional groups can also be used to modify the physicochemical and electronic properties of organic, inorganic, polymeric and biological materials. When compared to non-functionalized and non-passivated CQDs, surface-passivated CQDs have the advantage of being functionalized with desired molecules, making them a superior alternative to conventional organic dyes for specific applications in aqueous and non-aqueous solvents [Pan *et al.* (2010)]. These features make them superior in comparison to their competitors.

1.2.1. Synthesis of CQDs

A number of convenient, cost-efficient, size-controllable, and large-scale synthetic approaches have been developed since the discovery of CQDs. The general classification is divided into two categories: "top-down" and "bottom-up" techniques for CQDs synthesis as shown in (**Scheme 1.1**). Carbonaceous materials are cut or peeled off from bulk carbon

sources by chemical, electrochemical, or physical means. In this case, tiny organic molecules are pyrolyzed or carbonized to produce tiny aromatic molecules through stepwise chemical synthesis. CQDs have been made using various materials, including organic molecules, polymers, carbonaceous materials. In addition, there are a number of natural waste sources that can also be utilized for the synthesis of CQDs.



Scheme 1.1 An illustration of the techniques associated with the synthesis of fluorescence CQDs [Ngo *et al.* (2020)].

1.2.1.1. Top-down Approaches of Synthesis

Synthesis via top-down approaches can be viewed as a process of Nano-cutting, in which carbon macrostructures are destroyed into Nano dimensions by chemical reactions. For top-down processes, large carbon structures with sp^2 hybridization that lack efficient energy gaps or band gaps to display fluorescence feature were commonly used as starting materials. CQDs are typically fabricated with carbon materials such as graphite, Nano-diamonds, graphene oxide, carbon nanotubes, and carbon soot. The surface chemistry of the non-fluorescent bulk carbon structures, along with the size of the precursors, were optimized to produce fluorescent structures. Mainly, there are three top-down approaches: (i) Laser ablation; (ii) Arc discharge; and (iii) Electrochemical reaction

A. Laser ablation method

Laser ablation produces nanoparticles by irradiating the target surface with a high-energy laser pulse that induces a thermodynamic state in which high temperature and pressure are generated, the surface rapidly heats up and evaporates, and the vapour crystallizes into nanoparticles [Sun *et al.* (2006)]. A facile way to synthesize CQDs was described by Li *et al.* utilizing laser irradiation of carbon precursor, dispersed in an organic solvent [Li *et al.* (2010)]. Furthermore, Hu *et al.* demonstrated that by selecting the appropriate organic solvent during the laser irradiation process, the surface state of the CQDs can be modified to adjust the PL properties of the synthesized CQDs [Hu *et al.* (2009)]. CQDs with narrow size distributions, excellent water solubility, and good fluorescence properties can be prepared using laser ablation. Although its operation is complicated, and its cost is high, hence it is not widely used.

B. Arc Discharge Method

The fluorescent carbon particles were first discovered by Xu and team when they purified multiwall carbon nanotubes with electrophoretic arc discharge. In this study, Xu *et al.* isolated fluorescent carbon from crude multiwall carbon nanotubes soot by electrophoresis method. A fluorescent QY of 1.66 % was measured at 366 nm excitation wavelength [Xu *et al.* (2004)]. An additional experiment demonstrated that the surface of CQDs was attached to hydrophilic carboxyl groups. Since the discharge process produces particles of varying sizes of carbon, CQDs obtained with this technique have an excellent water solubility, but they generally have a wide particle size distribution. Due to their large particle size, CQDs would have a significantly decreased specific surface area, which may limit the number of active sites during electro catalysis.

C. Electrochemical method

Bulk carbon materials, such as CNTs, carbon fibres, graphite, etc., are commonly used as electrodes in electrochemical synthesis methods in the presence of an electrolyte solution. In order to achieve ultrapure CQDs, electrochemistry assisted fabrication is widely used. The most straightforward and convenient way to create CQDs is to do it under ambient pressure and temperature [Deng *et al.* (2014), Zhao *et al.* (2014), Anwar *et al.* (2019)]. Zhou and group used tetra-butyl ammonium perchlorate solution as the electrolyte to fabricate the first blue luminescent CQDs from multiwall CNTs [Zhou *et al.* (2007)]. Zheng and colleagues later developed water soluble CQDs with tuneable luminescence using graphite as an electrode material and buffering the pH with phosphate [Zheng *et al.* (2009)]. Hou and colleagues manufactured bright blue emitting CQDs in 2015 by treating urea and sodium citrate electrochemically in de-ionized water [Li *et al.* (2010)]. Similarly, electrochemical synthesis method is also effective for fabricating efficient electro-catalyst, but application of synthesized CQDs by such a method for electro-catalyst is rarely reported. So, the idea of integrating CQDs synthesis and electro-catalyst synthesis through one-pot electrochemical production is very intriguing.

1.2.1.2 Bottom-up Approaches of Synthesis

In bottom-up synthesis, a series of small molecules is polymerized or carbonized through different chemical reactions resulting in small clusters of reacting species that merge to form nanoparticles. Briefly, bottom-up methodologies involve carbonizing/pyrolyzing amino acids, polymers, carbohydrates and wastes, and then synthesising molecular species and assembling several aromatic hydrocarbon compounds. According to bottom-up synthesis, no specific prerequisites for the precursors are necessary, in contrast to top-down

synthesis techniques. Through the bottom-up route, any carbonaceous material can be tuned in to bright light from CQDs. For the large scale production of fluorescent CQDs, bottom-up synthesis has been considered the most productive strategy because of this flexibility [Huang *et al.* (2014)].

A. Thermal oxidation/Combustion method

At high temperatures, single molecules are broken down into simple substances through thermal/combustion reactions. In this reaction, the energy required to break the bonds in the substrate results in an endothermic reaction. Dehydration and carbonization of organic compounds can lead to the formation of small-sized CQDs [Peng *et al.* (2009)]. The first report of CQDs synthesis by combustion oxidation was published in 2007 by Liu *et al.* [Liu *et al.* (2007)]. During this synthesis, candle soot was collected by placing aluminium foil or a glass plate on top of a burning candle. In order to oxidize particle surfaces, the mixture was mixed with an oxidant and refluxed for 12 hours. Using centrifugation or dialysis, CQDs were cooled and collected, then subjected to electrophoresis using polyacrylamide gels. To synthesize CQDs, Ray *et al.* used candle soot that was refluxed with 5M hydrogen peroxide for 12 hours. By adding acetone to the suspension and centrifuging at 14000 rpm for 10 minutes, the particles suspended in solution were precipitated. The size separation was performed in a mixture of water, ethanol, and chloroform followed by high-speed and stepwise centrifugation. The carbon dots synthesized by combustion method have low QY, but they exhibit fluorescence without passivation.

B. Microwave Irradiation method

The microwave synthesis method is a microwave-heating method that carbonizes small organic molecules quickly. Zhu *et al.* used microwave pyrolysis to

synthesize CQDs by combining PEG-200 and saccharides such as glucose and fructose for the first time. Following a solution of the materials in water and heating in a microwave oven for 2–10 minutes, fluorescent CQDs were produced [Zhu *et al.* (2009)]. Glucose-derived CQDs were obtained by microwave pyrolysis, and according to Tang *et al.*, the diameter of the resulting CQDs is 1.65 nm [Tang *et al.* (2012)]. Xiao *et al.* synthesized fluorescent carbon nanoparticles from ionic liquids using microwave irradiation for the detection of quercetin [Xiao *et al.* (2013)]. By microwaving carbon nitride dots in the presence of acid, Liu *et al.* discovered that the presence of acid or alkali is crucial for obtaining fluorescent nanoparticles [Liu *et al.* (2012)]. This process is convenient and straightforward because carbon precursors are heated more rapidly, which results in a greater yield of carbon nanomaterial within a shorter period of time. Unfortunately, difficulties with separation, purification and non-uniform particle size limit the large-scale use of carbon Nano-materials.

C. Ultra-sonication Method

It has been proven that ultrasound can generate high pressure and low pressure waves in aqueous solution by synthesising and collapsing small vacuum bubbles. Cavitations are accompanied by the impinging of liquid jets at high speed, strong hydrodynamic shear forces, and de-agglomeration [Roshni *et al.* (2017), Wang *et al.* (2009), Zhang *et al.* (2015)]. Due to the ultrasonic waves, the larger organic precursors are cleaved, producing CQDs in the Nano-range. According to Li *et al.*, a mono dispersed water-soluble fluorescent carbon nanoparticle can be prepared in one step by ultra-sonication [Li *et al.* (2011)]. The carbon nanoparticles were synthesized by acid assisted ultra-sonication utilizing glucose and NaOH/HCl as molecular precursors. The obtained carbon nanoparticle exhibit an excitation

independent emission at 860 nm when excited at near infrared wavelengths of 700, 750, 800 and 850 nm [Li *et al.* (2011)]. Another Journal reported that CQDs synthesized by ultra-sonication of mustard seeds had a diameter between 3 and 10 nm [Roshni *et al.* (2017)]. The main drawback to this method is the rate at which sonochemical reduction occurs, is totally dependent on ultrasonic frequency [Jamkhande *et al.* (2019)].

D. Hydrothermal and solvothermal method

In Hydrothermal method, a reactor called a Teflon-line autoclave is used at high temperatures and pressures to react the various molecules in an aqueous solvent. In the first one-pot hydrothermal synthesis study, Zhang and the group produced CQDs whose average particle size was 2 nm and quantum yield was about 6.79 % through ascorbic acid in ethanol [Zhang *et al.* (2010)]. In 2013, Zhu and his colleagues synthesized highly fluorescent CQDs from citric acid and ethylenediamine using a hydrothermal route with considerable production yields, which proved to be potent biosensors for tracking ferric ions in cells [Zhu *et al.* (2013)]. It is a low-cost, environmentally friendly, and nontoxic way of synthesising novel carbon based materials. Hydrothermal method has multiple advantages, such as forming mono-dispersed and highly homogenous nanoparticles with controlled particle size distribution and morphology. Additionally, these carbon dots exhibit high QY without further oxidation or passivation, as well as high dispersibility in water, salt tolerance, and photo-bleaching resistance, which are favourable for mass production. The method has gained attention for the synthesis of CQDs in recent years due to its ease of use, reliable controllability, and the fact that the reaction occurs in closed vessels, which prevents the volatilization of toxic and harmful chemicals.

Unlike hydrothermal, solvothermal uses solvents, which represents a bit of a difference from hydrothermal. Solvents used in this process include ammonia, hydrogen peroxide, dimethylformamide, alcohol, and other inorganic and organic solvents.

1.2.2. Optical properties of CQDs

1.2.2.1 Absorption

CQDs prepared from various precursors and by different synthetic methods exhibit different UV-visible absorption properties. They show mainly absorption peak between 200-400 nm, with a tail extending to the visible range. A typical absorption band of CQDs in the UV-visible region is thought to be related to the $\pi-\pi^*$ transition of the conjugated carbon sp^2 and the $n-\pi^*$ transition of the hybridization with a heteroatoms [De *et al.* (2010)]. UV-visible absorption peaks of C-dots can be attributed to the presence of surface functional groups which occurs in the core part of the carbon structure.

1.2.2.2 Fluorescence

During photoluminescence, a molecule absorbs ultra violet-visible wavelengths of light, and come to be excited into a higher electronic state, and radiates light through longer wavelengths. This process occurs very rapidly, having a lifetime of approximately in nanosecond. There are two types of emission pathways: fluorescence and phosphorescence. Photons are emitted when the transition occurs from the excited singlet state (S_1) to the ground state at a longer wavelength are known as fluorescence, while as the phosphorescence refers to the photons are emitted when the transition occurs from the excited triplet state (T_1) to the ground state at a shorter wavelength. In comparison with fluorescence, phosphorescence peaks occur at longer wavelengths since of the lower energy of the triplet state. [Valeur *et al.* (2013)]. **Figure 1.2** shows the several electronic states of the molecule and the radiation transition between them in a representative Jablonski diagram.

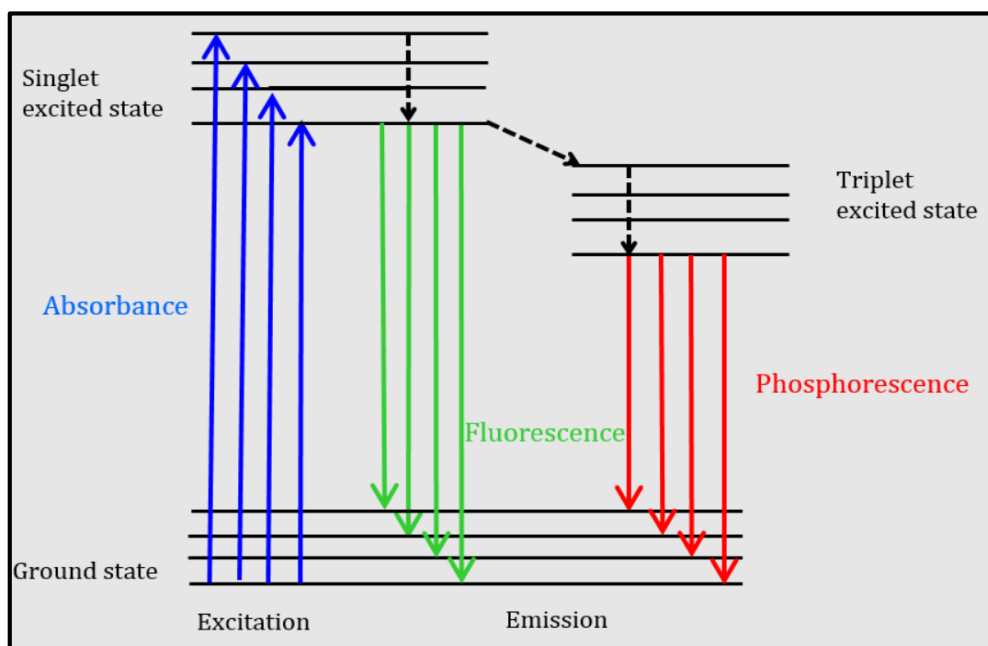


Figure 1.2 Illustration of fluorescence and phosphorescence in a Jablonski diagram.

A fascinating feature of CQDs is the fluorescence, both from a fundamental and an application perspective. In order to understand how CQDs emits fluorescence, many scientists have conducted extensive research across the world. Generally, in CQDs, fluorescence is generated by three main mechanisms. The first optical mechanism, where quantum confinement effects play a critical role in fluorescence, is controlled by quantum confinement or carbon core state. The second mechanism is surface mediated optical property which describes the fluorescence of carbon dots which is caused by surface defects. The last is that synergistic effect of quantum confinement and surface state insight the CQDs results from the existence different π -conjugated electrons islands. [Barman *et al.* (2013)].

The carbon core containing CQDs is commonly made from bulk materials counting graphene oxide, fullerene, graphene, and graphite which, reveal size-dependent fluorescence emission because of quantum confinement. **Figure 1.3** shows that small

nanoparticles cause a higher bandgap, resulting in different coloured emissions. As the size of nanoparticles decreases, the bandgap increases.

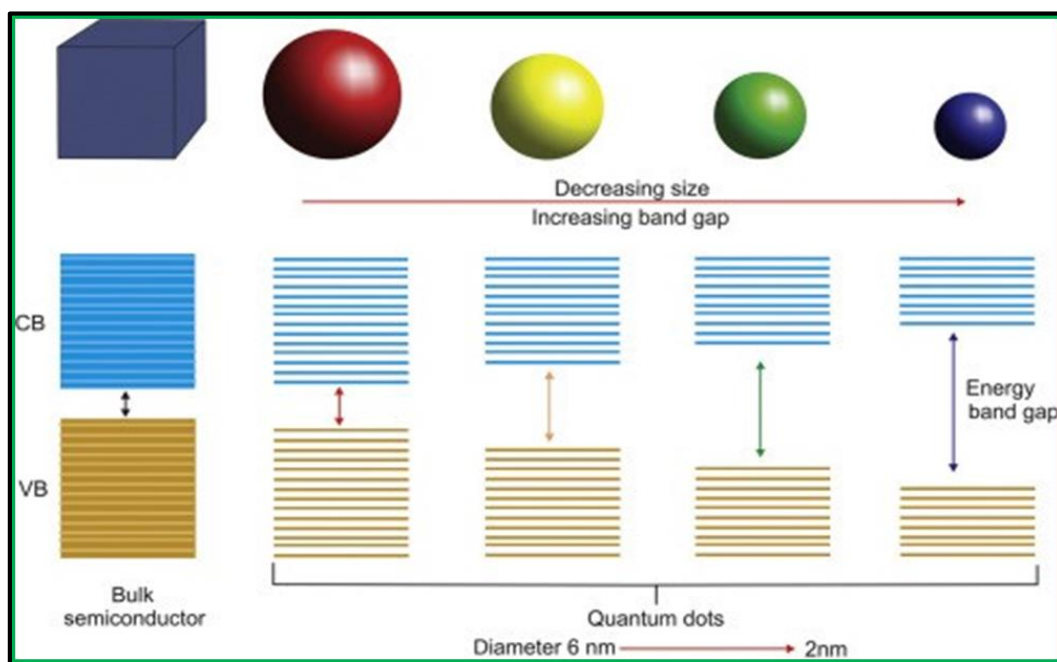


Figure 1.3 A reduction in nanoparticle size increases their energy band gap, resulting in different-coloured nanoparticles

The quantum confinement effect is also crucial for the fluorescence in the core shell of CQDs. The fluorescence arising from carbon core is caused by the band gap transition of conjugated π electrons that occur in the carbon domains. The sp^2 carbon clusters in the carbon core are dispersed in the sp^3 carbon skeleton [Sk *et al.* (2014), Kwon *et al.* (2014)]. Therefore, the optical properties of CQDs depend on the π -electron state of the sp^2 carbon cluster. As particle size increases, conjugated π domains also increase and the bandgap decreases. The red shift in emission is due to this reduction in bandgap. In this way, the fluorescence of CQDs can be tuned by adjusting the size of carbon core π domains. Using CA and urea precursors, Miao *et al.* synthesized multicolour emitting CQDs via thermal pyrolysis process, and the emission of CQDs can be tuned by tuning reaction conditions

such as the ratio of precursors and reaction temperature. Three different types of CQDs were produced, emitting blue, green, and red light, respectively [Miao *et al.* (2018)].

The surface state chemistry of CQDs plays an important role in studying fluorescence. The surface state is the spherical shell that surrounds CQDs, distinct from the core structure [Long *et al.* (2012)]. The degree of surface oxidation, emissive traps, and surface functional groups determine the surface state fluorescence. Alternatively, CQDs synthesized from small molecules exhibit excitation-dependent emission because they possess surface energy trap states, which can be tuned by modification of the surface. In contrast, Scrivens *et al.* found that the appearance of carbon dots depends on the particle size, while Sun *et al.* found that CQDs possess photophysical properties depending on their surface nature [Xu *et al.* (2004), Sun *et al.* (2006)]. Most studies find that CQDs emit fluorescence based on excitation, whereas there are few reports of emission from CQDs independent of excitation. According to Wei *et al.*, CQDs exhibit size independent tuneable fluorescence, whereas Teng's group demonstrated wavelength-independent excitation-dependent fluorescence [Yeh *et al.* (2016), Wei *et al.* (2015)].

Some studies have explained that the fluorescence of CQDs is caused by the combined effects of surface state and quantum confinement [Zhu *et al.* (2018)]. Increasing the size of CQDs leads to a larger conjugated π electron system, which is a cause of red-shifted emission, as reported by Bao *et al.* additionally, they had experimented with different degrees of surface oxidation, which resulted in narrowing the energy gap. They proposed that the fluorescence of CQDs might be originate from a synergistic effect between these two phenomena [Bao *et al.* (2015)]. With careful adjustment of the carbon core structure and changing the surface functionalities, Liu *et al.* were able to produce full-colour emitting CQDs [Xue *et al.* (2018)].

1.2.2.3. Phosphorescence

Phosphorescence is the slow emission of light from absorbed light by materials. It's a forbidden transition between the lowest triplet excitation state (T_1) and singlet ground state (S_0) according to the spin selection rule in quantum mechanics (**Figure. 1.2**). In general, it is found that the energy gap between singlet excited state (S_1) and triplet excited state (T_1) of pure luminescent material is large, which inhibits intersystem crossing (ISC), leading to fluorescence rather than phosphorescence. In contrast, because of spin-orbit coupling by heavy metal atoms, the rate of intersystem crossing (ISC) is enhanced, leading to strong room temperature phosphorescence (RTP). By dispersing carbon dots into polyvinyl alcohol matrix, Deng *et al.* reported the first phosphorescence properties of carbon dots in 2013 [Deng *et al.* (2013)]. Composite material exhibits a 500 nm emission peak with an average lifetime of 380 at 325 nm excitation. It is suggested that phosphorescence in carbon quantum dots results from the aromatic carbonyl groups and from the polyvinyl alcohol matrix, in which the singlet state and the triplet state are close in energy to facilitate spin-orbit coupling, leading to the appearance of phosphorescence.

1.2.3. The influence of doping on the fluorescence properties of CQDs

Un-doped CQDs, have a low fluorescence efficiency after surface functionalization and passivation compared to conventional semiconductor quantum dots, are made up of hydrogen, oxygen and major carbon atoms. Carbon atoms of the un-doped CQDs in sp^2 & sp^3 configurations at the altering proportions. To expand the use of un-doped CQDs in biological and analytical applications, it must be needed to improve their fluorescent properties. Therefore, doping is an efficient method to improve quantum yield, water solubility, fluorescent properties, as well as other physicochemical properties of un-doped

CQDs. According to earlier reports, both metal and non-metal or heteroatoms could be used for doping. Doping of metals and non-metals into CQDs would influence the interaction between the π - and n -states depending on the extent of orbital overlap and electron withdrawing/donating abilities of the heteroatoms [Lombardo *et al.* (2020)]. Metal doping, however, results in toxicity in CQDs which limits their potential biological applications, while heteroatom doping or non-metal has attracted much interest in recent years. CQDs may either be doped with heteroatoms or co-doped to improve their fluorescence properties and ultimately facilitate their various applications.

1.2.3.1. Single heteroatom doping

A. N-Doped CQDs

The N-doped CQDs enhances the surface-state defects and their chemical and electrical properties by providing reactive functional groups such as -OH, -COOH, -N=C-, -CN, -NH₂. Hence, these reactive functional moieties enhance quantum yield of CQDs. As an inexpensive source for synthesis and in situ doping of carbon dots, naturally occurring precursors such as amino acids, proteins, fruit peels, fish remains, coconut shells, and organic waste are readily available. Furthermore, pure organic compounds can be doped with ammonia, ethylenediamine, nitric acid, sulphuric acid, and phosphoric acid, among others, to produce highly fluorescent heteroatom doped carbon dots. At first, Liu *et al.* developed N-doped CQDs with blue emission via hydrothermal treatment of a natural resource, where they observed an increase in QY from 2.5 to 6.2% with decreasing size from 22 to 2 nm [Liu *et al.* (2012)]. In a previous study, Dey *et al.* synthesised blue-light emitting CQDs by reacting glucose and urea; however, that process resulted in a QY of 0.7 and 1% respectively [Dey *et al.* (2014)]. The researchers in another study have utilized folic acid as the starting material to prepare N-doped CQDs that emit blue light after being hydrothermally treated for 2 h at 150 °C, where these CQDs have possessed 23% QY

[Wang *et al.* (2014)]. According to Jiang *et al.* 1,2,4-triaminobenzene was used as both C and N sources (self-doping) in a hydrothermal process at 120 °C for 12 h to prepare N-doped CQDs [Jiang *et al.* (2015)]. A similar approach was employed by Ji *et al.* to prepare N-doped CQDs via hydrothermal reaction at 260 °C for 24 h using polyacrylamide as a source of C and N [V *et al.* (2016)]. In another study, the authors have also prepared N-doped CQDs with a higher QY of 80% through the hydrothermal reaction of citric acid and ethylenediamine while optimizing their reaction temperatures to 150, 200, 250, and 300 °C for 5 h [Zhu *et al.* (2013)].

B. S-Doped CQDs

S doping increases emission intensity substantially by adjusting the electron density of neighbouring carbon atoms, even though it has been relatively less reported than N doping. CQDs doped with sulphur can be synthesized using different sulphur sources, such as thiomalic acid, sulphuric acid, and L-cysteine. For the first time, Chandra *et al.* fabricated S-doped carbon dots without surface passivation using thiomalic acid [Chandra *et al.* (2013)]. In another study, Xu *et al.* synthesized S-doped CQDs by a straightforward hydrothermal method using sodium citrate solution and sodium thiosulfate. The synthesised S-doped CQDs exhibited unique emission behaviour and exhibited a high fluorescence quantum yield of 67% [Xu *et al.* (2015)]. Through carbonization, Hu *et al.* synthesized S-doped CQDs using concentrated sulphuric acid and waste cooking oil. This produces a bright ultraviolet emission of 378 nm in S-doped CQDs with a band gap of 3.28 eV [Hu *et al.* (2014)]. Later, Rahmayanti *et al.* prepared S-doped CQDs by simply heating precursor citric acid and urea with sulphur deposits [Dany Rahmayanti *et al.* (2015)]. In another recent study, Wu *et al.* (2018) successfully prepared S-doped CQDs with blue emission and QY of 4.4% via a hydrothermal strategy at 200 °C for 12 hours using Vitamin B1 (thiamine hydrochloride) and ethylenediamine [Wu *et al.* (2018)].

C. B-Doped CQDs

The n-type dopants N, P, and S can enhance electron concentration within CQDs. Nonetheless, CQDs conferred by B-doping have distinct characteristics [Wang *et al.* (2016)]. Because the B–C bond is 0.5% longer than the C–C bond, a defect in the energy state of CQDs is created by the electronic defect in B, resulting in emissions from defects on their surfaces. The effect of B-doping is to generate a large number of active sites on a CQD, thereby changing its optical properties [Zhou *et al.* (2017)]. The B-doped CQDs were fabricated by Shan *et al.* using a solvothermal process at 200°C for 2 h using boron tribromide, as the B dopant, and hydroquinone as the C precursor [Shan *et al.* (2014)]. Then, aqueous solutions of citric acid, boric acid, and urea were microwave heated by Bourlinos *et al.*, which lead to the formation of B-doped CQDs whose excitation at 350 nm produces a band at 450 nm corresponding to a blue photoluminescence with a quantum yield of 10-15% [Bourlinos *et al.* (2015)]. Furthermore, Jia *et al.* have prepared B-doped CQDs by hydrothermal method at 200 °C for 10 h by using phenylboronic acid as carbon and B sources. Their CQDs display excitation/emission wavelengths of 247/323 nm and have an improved QY of about 12% [Jia *et al.* (2019)].

D. P-Doped CQDs

Although P has a larger atomic radius than C, P-doping in diamond films can cause substituted defects. Thus, P acts as n-type donor and enhances the photoelectric properties of CQDs. In addition, P doping process increases the number of active sites in CQDs, improving their fluorescence properties, while also modifying their electronic properties. [Zhou *et al.* (2014)]. Zhou *et al.* synthesized P-doped CQDs by solvent thermal process, using phosphorus tribromide and hydroquinone precursors, with very efficient fluorescence. P-doped CQDs could alter their

electronic characteristics and offer more active sites, thus are expected to produce new properties and potential applications in catalysis and photovoltaic [Zhou *et al.* (2014)]. In another study, Shi *et al.* prepared P-doped CQDs using sucrose and phosphoric acid as precursors, and then hydrothermally heated at 200 °C for 5 hours, with a 21.8% quantum yield [Shi *et al.* (2015)]. Sarkar *et al.*, however, synthesized blue amino acid-functionalized and green P-doped CQDs by using the thermal coupling between citric acid and the Na-salt of glycine, L-valine, and L-isolucine in the presence of sodium dihydrogen phosphate. Sodium dihydrogen phosphate is used as the P source in this example [Sarkar *et al.* (2015)]. Recently, the fluorescent P-doped CQDs were synthesized by Yang *et al.* by hydrothermal treatment at 160, 200, or 240 °C for 4 h using phytic acid and sodium citrate as precursors [Yang *et al.* (2018)].

Thus, single hetero atom doping is capable of significantly improving the emission properties by effectively stabilizing the excitons of the CQDs, which will passivate the surface active sites. For CQDs to achieve high fluorescence efficiency or QY, the percentage of doped atoms is important. Higher heteroatom content traps more electrons and causes more surface states to form on doped CQDs, leading to a high fluorescence quantum yield.

1.2.3.2. Co-doping of multiple heteroatoms

In co-doping, more than one heteroatom is present on the CQD surface. It is possible to enhance the electronic properties of CQDs and extend their applications in fields like drug delivery, chemical sensing, bio-sensing, photovoltaic devices, and photo catalysis due to the distinctive electronic arrangement and collective tendency of individual heteroatoms.

A. N and S co-doped CQDs (NS-CQDs)

The properties of S and N can complement each other by cooperating to provide electrons, support radiation recombination, and enhance the fluorescence quantum yield of CQDs, thereby enhancing their properties. First, Dong *et al.* synthesised NS-CQDs through a one-step hydrothermal method using citric acid and L-cysteine as precursors [Dong *et al.* (2013)]. Here, L-cysteine provided nitrogen and sulphur, while citric acid provided carbon. NS-CQDs synthesized in this study displayed an excitation-independent emission behaviour, as well as a very high fluorescence quantum yield of 73%. In another study, Zhao and Zhang prepared NS-CQDs with ultra-high quantum yield by following the same route and using different sulphur and nitrogen sources [Xue *et al.* (2016), Wang *et al.* (2016)]. By using ammonium thiocyanate as the sulphur and nitrogen source, Zhao and co-workers synthesized NS-CQDs with a fluorescence quantum yield of 74.15 %, while Zhang and co-workers successfully synthesized co-doped NS-CQDs with a fluorescence quantum yield of 73.1%. Besides, Xiong *et al.* demonstrated the use of the hydrothermal method to produce NS-CQDs using a lipoic acid, which show excitation-dependent emission, good fluorescent stability, and low toxicity. The resultant NS-CQDs have an average particle size of 2.7 nm and a fluorescence quantum yield of 54.4% [Ding *et al.* (2014)].

B. N and P co-doped CQDs (NP-CQDs)

Due to the combined benefits of both N and P atoms, co-doping N and P atoms into CQDs is likely to produce new, unexpected properties in the co-doped CQDs. Firstly, Sahu *et al.* used citric acid and di-ammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$ as precursors in a ratio of 1:4 to produce N and P co-doped CQDs via single step hydrothermal synthesis [Chandra *et al.* (2016)]. The particle size of NP-CQDs ranged from 1.5 to 4 nm and 59% of the quantum yield was attained in this study. Zhang *et al.* also used a similar strategy,

leading to NP-CQDs with a fluorescence QY of 23.5% and strong blue fluorescence upon 340 nm excitation [Gong *et al.* (2016)]. For the synthesis of the NP-CDs with dual emission nature, Sun *et al.* used aniline as a carbon source and ethylenediamine with phosphoric acid as N and P sources. Under different excitation wavelengths, as-prepared NP-CQDs exhibited a bright dual emission which emitted a strong green and blue fluorescence, with QY of 51 % and 38 %, respectively [Sun *et al.* (2015)]. More recently, Zhao *et al.* have synthesized NP-CQDs via a one-pot hydrothermal synthesis method, which prevents the use of high-temperature conditions and uses glucose, ammonia, and phosphoric acid as precursors [Shi *et al.* (2016)]. Feng *et al.* recently presented a sensitive way to detect cocaine by using fluorescent NP-CQDs. NP-CQDs are being synthesized using simple hydrothermal treatment with citric acid, phosphoric acid and ethylenediamine precursors [Liu *et al.* (2022)].

C. N and B co-doped CQDs (NB-CQDs)

In the periodic table, boron is the left-hand neighbour of carbon, while nitrogen is the right neighbour. The carbon-based nanomaterial needs not only to be doped with its two neighbours but also doped on a practical level [Jana *et al.* (2013)]. A blue-emitting B and N co-doped CQD was synthesized by Liu *et al.* using polyethylenimine (PEI) and 4-formylphenylboronic acid precursors in a hydrothermal reaction at 220 °C for 8 h, achieving a QY of 15.85% [Liu *et al.* (2017)]. In an analogous study, Ye *et al.* synthesized three altered blue-emitting NB-CQDs with sodium tetraborate, citric acid, boric acid, ethylenediamine, and manganese borate under hydrothermal conditions for four hours, resulting in QY values of 29.01%, 51.42%, and 68.28%, respectively [Ye *et al.* (2016)]. Guo *et al.* synthesized yellow-green NB-CQDs by hydrothermal synthesis at 180 °C for 12 h using 2-hydroxyphenylboronic acid and ethylenediamine with a QY of 6.59% [Guo *et al.* (2017)]. Huang *et al.* obtained boron and nitrogen doped CQDs using a one-pot

hydrothermal method at 160 degree C for 7 hours by 1,2-ethylenediamine and 3-aminobenzeneboronic acid with a QY of 47% [Huang *et al.* (2018)]. Recently, Xiao *et al.* employed hydrothermal method at 160 degree C for 8 h to synthesize NB-CQDs with blue fluorescence radiation from three aminophenylboronic acid isomers [Xiao *et al.* (2018)].

D. B and S co-doped CQDs (BS-CQDs)

Using poly (sodium-p-styrenesulfonate) and borax as the S and B sources, Zhao *et al.* reported hydrothermal synthesis process for BS-CQDs with a QY of 25.7%. [Zhao *et al.* (2018)]. According to this study, the maximum excitation and emission wavelengths of BS-CQDs are 250 nm and 308 nm, respectively. Similarly, the large blue shift in emission from B and S doped CQDs was accredited to boron's strong electron-withdrawal ability.

1.3 Fluorescence Quantum Yield

According to equation, the fluorescence quantum yield equals the ratio of photons emitted to photons absorbed. A typical value of QY will be less than one because the absorption of all photons does not result in the formation of product. The value of QY, however, may be greater than one when the reaction is induced by photons or radiation.

$$\text{Quantum yield (QY)} = \frac{\text{Photon emitted}}{\text{Photon absorbed}} \quad 1.1$$

It is determined by comparing the quantum yield of the fluorophore materials with the quantum yield of the standard fluorophore materials.

1.4 An overview of Fluorescence quenching

Fluorescence intensity of fluorophore materials is reduced upon interaction with specific molecules or analytes in quenching. There are several types of chemical quenchers, including iodide ions, acrylamide and molecular oxygen [Phillips *et al.* (1986)]. Several processes can cause quenching, including inner filter effect (IFE), static quenching, dynamic quenching, Fluorescence resonance energy transfer (FRET) or other mechanisms

depending on the interaction between the quencher and the fluorophore. Basically in IFE, the absorption spectra of the analyte material overlap with the emission spectra of the fluorophore materials, as analyte molecules (quenchers) re-absorb the emitted light [Yuan *et al.* (1987)]. In general, toxic metal ions with broad absorption spectra exhibit IFE mechanisms. Despite this, the static quenching mechanism occurs when the fluorescence of fluorophores is quenched by a complex formation between the quencher and fluorophores [Feng *et al.* (2016)]. Accordingly, fluorescence follows the following equation when quenched with a specified concentration of quencher.

$$F_0/F = 1 + K_{sv} [Q] \quad 1.2$$

This equation contains F_0 and F as fluorescent intensities of fluorophores in the presence and absence of quenching molecules, $[Q]$ as the quencher concentration, and K_{sv} as the Stern-Volmer quenching constant, respectively. Additionally, with static quenching the lifetime of fluorescence is not changed as a result of the presence of the quencher molecule, which indicates that there is a ground state interaction between the fluorophore and quencher molecule. Further, as the temperature increases, the quenching constant (K_{sv}) decreases.

The dynamic quenching process is also referred to as collisional quenching, in which the fluorescence intensity of the fluorophore diminishes by the interaction of the quenchers with the fluorophores. As quencher molecules are present, the fluorescence lifetime of fluorophore is decreased, whereas as the temperature is raised, the Stern-Volmer constant (K_{sv}) increases because the diffusion rate increases.

A fluorophore acts as a donor in fluorescence resonance energy transfer, while an analyte acts as an acceptor. Energy transfer interactions take place when the emission spectrum of the donor and the absorption spectrum of the acceptor overlap. The fluorescence of the fluorophore is quenched. The fluorophore and analyte must be less than 10 nm apart for

this type of interaction to occur. In a recent study, Chatzimarkou *et al.* synthesized nitrogen-doped carbon dots with intense blue fluorescence, which was effectively quenched by 4-nitrophenol through the FRET mechanism with a limit of detection of 13 nm [Chatzimarkou *et al.* (2018)]. Ganiga *et al.* developed a FRET-based sensor platform to detect ammonia with a limit of detection of 3 ppm using carbon dots as a signal transducer and sodium rhodizonate as an analyte-specific molecule [Ganiga *et al.* (2016)]. Recently, Apak *et al.* synthesized N-CQDs using ethylenediamine, diaminocyclohexane and citric acid for the detection of 2,4,6-Trinitrotoluene through FRET mechanism through a limit of detection of 30 nm [Koç *et al.* (2022)].

1.5. Applications of CQDs

It is well-known that CQDs have excellent properties, including tuneable high electrical conductivity, excellent water solubility, high fluorescence, good surface-to-volume ratio, photo-stability, and less toxic, which made them suitable for bio-sensing, chemical sensing, photo-catalysis, bio-imaging, drug delivery and optoelectronics.

1.5.1. Biosensing

CQDs-based biosensors are perfect for the monitoring of glucose, cellular copper, iron, pH, phosphate, and nucleic acid because of their high solubility in water, excellent biocompatibility, nontoxicity, flexible surface modifications, and high cell permeability [Shi *et al.* (2011), Zhu *et al.* (2011), Shi *et al.* (2012), Zhu *et al.* (2013), Zhao *et al.* (2011), Li *et al.* (2011)]. The quenching was also used to detection of nucleic acids with high selectivity that even a single base divergence could be detected. First, a fluorescent dye-labelled single-stranded DNA (ss-DNA) was adsorbed onto a CQD by π - π interaction, successfully quenching the dye. The freshly produced double-stranded DNA desorbed from the CQD surface, but fluorescence was restored when the ss-DNA hybridised with the

target. [Li *et al.* (2011)]. This application has a lot of promise for detecting single-nucleotide polymorphisms based on dissimilarities in emission intensity. CQDs were also utilised to identify bacterial cells in sewage water [Mandal *et al.* (2011)], as well as small bio-analytes such as dopamine [Qu *et al.* (2013)], glucose [Singh *et al.* (2018)], ascorbic acid [Zhang *et al.* (2022)], antibacterial medicines, mitochondrial H₂O₂ [Du *et al.* (2014)], *E. coli* [Hu *et al.* (2021)], and others.

1.5.2. Chemical sensing

CQDs are eminent in their ability to modify the surface, to be non-toxic, and to be water soluble, making them an effective and efficient way to determine the toxicity of nitro compounds, pesticides, hazardous metals ions (Cr⁶⁺, Cd²⁺, Hg²⁺, Pd²⁺, As⁵⁺) and other compounds. To date, CQDs are one of the most common probes used to detect explosives based nitroaromatics and pesticides. Some nitro compounds, such as 2,4,6-trinitrophenol (picric acid), 2,4,6-trinitrotoluene, trinitrotriazine (RDX), 2,4-dinitrotoluene, Nitrobenzene, o-, m-, and p-dinitrobenzene, and 1,3,5-trinitrobenzene have been investigated. For example, Tian *et al.* used a hydrothermal technique to synthesis CQDs for detecting TNT residues in groundwater, with a detection limit of 0.213 mol/L [Tian *et al.* (2017)]. Khan *et al.* developed NS-CQDs using L-Lysine and thiourea as precursors for the detection of picric acid with a limit of detection of 0.24 0.24 μM [Khan *et al.* (2020)]. Chandra *et al.* synthesised NS-CQDs from citric acid and thiosemicarbazide as precursors, which they utilized as a nanoprobe for Picric acid detection with a good limit of detection of 0.22 μM [Chandra *et al.* (2020)].

CQDs have also been used in the detection of pesticides in recent years. Minimum concentration of pesticides may be present in the environmental samples, causing health problems to humans; hence, it is important to trace them effectively. In a recent

investigation, Li *et al.* used an ultrasonic approach to synthesis NS-CQDs from an ionic liquid source, which they used in a two-enzyme system for pesticide (carbaryl) detection. The enzyme-produced H_2O_2 effectively reduces the fluorescence intensity of the NS-CQDs, resulting in a highly sensitive detector with a limit of detection as low as 5 ppb [Li *et al.* (2016)]. Wu *et al.* developed CQDs to detect organophosphate (paraxon) concentrations in the range of $0.05\text{--}50\ \mu\text{g L}^{-1}$, with a detection limit of $0.05\ \mu\text{g L}^{-1}$. The fluorescence emission of CQDs could be efficiently quenched by AuNPs, and the quenched fluorescence could later be recovered using thiocholine [Wu *et al.* (2017)]. Recently, Chandra *et al.* synthesised CQDs from Jatropha fruits by hydrothermal method at $180\ ^\circ\text{C}$ for 5 h. In this study, the synthesised nanoprobe was used for the detection of chlorpyrifos and shown satisfactory limit of detection of $2.7\ \text{ng/mL}$ with a linear range of $0.02\text{--}0.18\ \mu\text{g/mL}$ [Chandra *et al.* (2022)].

1.5.3 Photocatalysis

Photo-catalytically active nanomaterials have been used to accelerate light-energy conversion so that photocatalysis has risen to become a popular application of solar energy. In recent years, CQDs have been used as photocatalysts for pollutants degradation [Han *et al.* (2020), Xu *et al.* (2019)], CO_2 reduction [Yan *et al.* (2018)], water splitting [Sarma *et al.* (2019)], and chemical reactions [Bhattacharyya *et al.* (2017)] in solar energy conversion due to their properties such as broad absorption from UV to NIR, excellent photo-stability, low costs, and charge separation. Nitrogen-enriched CQDs enhance photocatalytic hydrogen generation from water by improving electron transfer [Bhattacharyya *et al.* (2017)]. In general, CQDs are used to design more efficient photocatalysts with semiconductor nanomaterials such as TiO_2 [Zhang *et al.* (2013)], CdS [Li *et al.* (2014)], Bi_2WO_6 [Di *et al.* (2015)], Ag_3PO_4 [Zhang *et al.* (2012)], Cu_2O [Li *et al.* (2012)], and Fe_2O_3

[Zhang *et al.* (2011)] performing as electron acceptor in the hetero-junction to enhance photocatalytic efficiency. For example, Yang's research group were established the integration of CQDs into the g-C₃N₄ backbone amplified carrier transport in inter or intra-sheets and concentrated recombination, thereby improving the photocatalytic degradation of Rhodamine B. Moreover, increasing the efficiency of photocatalytic CO₂ reduction and water splitting for H₂ evolution [Han *et al.* (2020)]. In a similar way, a CQDs/TiO₂ composite nanomaterial was synthesized and its photoelectrochemical properties and photocatalytic activity were investigated. Under visible light irradiation, CQD-sensitized TiO₂ composites have enhanced photocurrent and photo-potential, with 2.7 times higher photocurrent density than pristine TiO₂ nanomaterial. Consequently, the degradation efficiency of methylene blue using CQDs/TiO₂ nanotubes is about 14% higher than that of using pristine TiO₂ nanomaterial [Sun *et al.* (2014)]. Chemically manipulated CQDs or doped CQDs can be used as photocatalysts for green chemistry and energy. Researchers are recommending the usage of CQD-based photocatalysts for environmental remediation and solar energy utilization in the near future.

1.5.4. Bio-imaging

In research and clinical importance, bio-imaging grow into progressively to observe and appreciate biological practises in vivo and in vitro [Zhao *et al.* (2017)]. In addition to being nontoxic and environmentally friendly, carbon is also an excellent material for bio-imaging probes to detect several diseases and observer performance. [Yang *et al.* (2009)]. Since semiconductor quantum dots and various organic dyes are fluorescent, they are widely used as staining agents. In bio-imaging studies, their use is quite complicated and not recommended due to metal toxicity and weak fluorescent properties [Zhu *et al.* (2013)]. Recent studies suggest that CQDs are a class of fluorescent materials with distinctive

optical properties that can be treat several disease in biological systems via bio-imaging [Cao *et al.* (2007)]. Considering these important influences, CQDs have emerged as the most desirable material for their chemical inertness, biocompatibility and solubility. [Liu *et al.* (2020)]. Liu *et al.* synthesized CQDs from carbon nanotubes and graphite, and they demonstrated vivo fluorescence imaging in mouse experiments using a variation of wavelengths, including some in the near-infrared region. Further, CQDs were studied in vivo for bio distribution and toxicity in mice over different periods of time. The treated animals showed no observable signs of toxicity [Tao *et al.* (2012)]. To test the expediency of the synthesized CQDs for bio-imaging, Hsu *et al.* used pig kidney cells (LLC-PK1) for the further investigation [Hsu *et al.* (2012)]. Further, using orange juice to synthesize CQDs, Sahu *et al.* recently investigated the in vitro bioimaging of human osteosarcoma (MG-63) cells [Sahu *et al.* (2012)]. CQDs were internalized by endocytosis in both cases, and were found both within the cells cytoplasm and their membrane. Wu *et al.*, developed fluorescent CQDs from bombyx mori silk and further used for bio-imaging investigation on human lung cancer (A 549) cells, finding that the CQDs penetrated in to the cell's nucleus through nuclear pores, thus lightening the entire cell [Wu *et al.* (2013)]. Recently, Phosphorus or nitrogen doped CQDs displayed outstanding photo-stability, low toxicity, and respectable biocompatibility, making them ideal for use as fluorescent investigations in bio-imaging for the detection of PC-12 cancer cells [Wang *et al.* (2021)].

1.5.5. Drug delivery

Recent research studies have shown that CQDs possess excellent optical property and drug-loading capability, which makes them a promising class of drug carriers for a wide range of biomedical applications and biocompatibility [Cohen *et al.* (2014)]. Due to their excellent drug delivery capabilities, CQDs are gaining more and more attention from

researchers. Contrast agents such as CQDs are safe and biocompatible, and they help to facilitate the release of drugs that are insoluble in water. Interestingly, CQDs can be loaded with drugs through π - π stacking to also improve their solubility, improve tumour retention, and reduce their side effects [Miao *et al.* (2017), Zhou *et al.* (2011), Su *et al.* (2020)]. In recent years, several scientists have developed carbon-based quantum dots for numerous drug delivery systems. For instance, Ding and colleagues developed a theragnostic agent that loaded anticancer drug DOX onto quantum dots surface and attached fluorescent Cy dye using a cathepsin D-responsive P peptide [Ding *et al.* (2017)]. Pietro *et al.* synthesized GQDs to deliver conventional chemotherapeutics with greater efficiency, since their activity is restricted by resistance mechanisms and dose-limiting side effects. They found that GQDs were highly biocompatible and are capable of releasing drugs into cancer cells [Iannazzo *et al.* (2017)]. For another example, Samimi and colleagues synthesized quinic acid based CQDs for drug delivery system of gemcitabine to breast cancer cells [Samimi *et al.* (2021)] and so on.

Moreover, functionalized CQDs reduce cytotoxicity by preventing leakage of drugs into normal cells. On the surface of functionalized CQDs, amino groups function as points of crosslinking for tumour theragnostics. CQDs was synthesized via microwave pyrolysis through Citric acid precursor followed by crosslinking with PEGylated oxidized alginate conjugated with therapeutic doxorubicin via acid-labile Schiff base linkage. [Li *et al.* (2020)]. Based on the in vitro trial results, theragnostic nanoparticles release drugs without bursts in a pH-dependent manner in an acidic microenvironment. In addition, their emission property enabled imaging-guided drug delivery [Jia *et al.* (2016)]. In addition, CQDs have been used for targeting specific regions of the body, including the nucleus and mitochondria [Wu *et al.* (2017)]. Recently, Hua *et al.* synthesised CQDs from chitosan, mercaptosuccinic acid and ethylenediamine by hydrothermal procedure were establish to have long-term

imaging in contrast to commercially accessible MitoTracker dye, temperature-dependent transport, and receptor-mediated endocytosis [Hua *et al.* (2018)].

1.5.6. Optoelectronics

Several unique properties of CQDs have attracted attention for their use in optoelectronic devices, such as high specific surface areas, ultrafast electron extraction, long hot electron lifetime, high electron mobility, tuneable bandgaps, strong stable fluorescence, low cost, and non-toxicity. In optoelectronic applications, several research scientists have used CQDs to fabricate light-emitting diodes (LED), solar cells, and solar fuels. In recent years, many researchers have studied LEDs to determine their potential applications in liquid crystal displays, full-colour display industry, and as the next generation of lighting sources for our daily life [Kwak *et al.* (2012)]. CQDs may offer an auspicious substitute to rare phosphors and toxic based metal semiconductor QDs in LEDs because their tuneable emission properties, minimum cost and not environmentally harmful make them an attractive option [Sun *et al.* (2007)]. Unlike rare earth-based phosphors and toxic metal-based QDs, CQDs promise to be a more cost-effective alternative to LEDs. Furthermore, several researchers have demonstrated that CQDs embedded in solid matrices such as silicone [Feng *et al.* (2015)], starch [Sun *et al.* (2014)], resin [Zhang *et al.* (2015)] and cellulose nanofiber [Tetsuka *et al.* (2015)] can retain their fluorescence in order to avoid aggregation-induced quenching in CQDs. Recently, Chen *et al.* fabricated blue, orange, and white LEDs with UV chips by unzipping epoxy-enriched polystyrene photonic crystals with varying temperatures and found fluorescence QY of up to 47% with a colour coordinates of 0.45, 0.44 [Guo *et al.* (2012)]. In another study, Chen *et al.* discussed about white LEDs which was produced from combining yellow-emitting CQDs and blue GaN-based LED chips. This device emits warm white light with the colour coordinates of (0.34,

0.35), which is close to balanced white-light emission coordinates (0.33, 0.33) [Chen *et al.* (2013)].

Furthermore, CQDs have been investigated widely in solar cells, where their distinctive optical properties, functional moieties such as hydroxyl, carboxyl, amino, and high electron mobility have been shown to improve efficiency. In solar cells, CQDs have several roles. They facilitate separation of photo-generated electron-hole pairs, and at the same time broaden the spectrum of light absorption, suppress carrier recombination and enhance the environmental stability of the device. In recent study, Zhang *et al.* reported that N-CQDs, as sensitizers, are used in photo-catalysts and dye-sensitized solar cells containing TiO₂-based composite photo-catalysts [Zhang *et al.* (2013)]. Wang *et al.* have developed a similar model of solar cells (DSSC) by sandwiching a platinum (Pt) counter electrode between a TiO₂ electrode sensitized N-CQDs [Wang *et al.* (2016)].

1.5.7. Peroxidase-like mimetic activity

Peroxidase is an enzyme that is naturally occurring in horseradish roots and catalyses oxidation reactions using hydrogen peroxide in ecosystems, as well as being used in biochemistry. There are numerous disadvantages to using natural enzymes, such as denaturation under harsh conditions and expensive purification and preservation. Therefore, it is urgent to develop an artificial enzyme that mimics nature. [Chen *et al.* (2013), Hosseini *et al.* (2017)]. Furthermore, artificial enzymes are low-cost, highly stable, non-toxic, eco-friendly, convenient, as well as easy to prepare. In the past few decades, numerous research groups have previously reported the use of iron oxide-based nanomaterials [Yu *et al.* (2009)], cerium-based nanomaterials [Asati *et al.* (2009)], Schiff base complexes [Maneiro *et al.* (2003)] and metal organic frameworks [Dong *et al.* (2017)] to show the mimic activity. In contrast, these nanomaterials are synthesised from toxic

substances, metal ions, and costly reagents, which have detrimental effects on human fitness and the surroundings. [Wei *et al.* (2008), Pal *et al.* (2018)]. Research has recently focused on developing commercial and sustainable synthesis procedures for carbon nanomaterials for example carbon quantum dots, graphene quantum dots, and carbon nanotubes that are analogous to natural enzymes in their peroxidase-like activity. [Song *et al.* (2010), Shi *et al.* (2011), Wu *et al.* (2014), Tripathi *et al.* (2020)]. These nanomaterials exhibit low cytotoxicity, excellent biocompatibility, high substrate specificity, high surface area, and unique excitation-dependent fluorescence properties [Shamsipur *et al.* (2018), Amin *et al.* (2018)]. Furthermore, fluorescent CQDs based peroxidase substrate oxidation provides an efficient tool for the detection of various biologically active molecules, including ascorbic acid, glucose, glutathione, amino acids, etc. For example, Vikas *et al.* demonstrated the mimetic activity for colorimetric detection of H₂O₂ and glutathione in human blood serum [Singh *et al.* (2018)]. In another example, The M-CQDs synthesized by Subhash *et al.* under hydrothermal conditions at 180°C for 3 hours revealed peroxidase-like activity for the detection of H₂O₂ and ascorbic acid. [Chandra *et al.* (2019)].

1.6. Motivation of the study

Fluorescent CQDs have received much attention from researchers being alternatives to poisonous metal established semiconductor quantum dots attributable to their interesting optical properties, excellent biocompatibility, high aqueous solubility, tuneable fluorescence, photo stability, high electrical conductivity, and non-toxicity. CQDs are being manufactured increasingly using natural products and chemicals as an alternative of conventional, expensive chemical reagents not only for their availability, low price, and low carbonisation temperature, but also because of their natural lack of toxicity. Several reports indicate that CQDs synthesized from chemicals and natural products do not need surface functionalization. Thus, it is very important to search for cheap chemicals and

abundantly available natural products for the synthesis of CQDs. In order to obtain high fluorescence quantum yield, we adopted a bottom-up approach using the hydrothermal method since it is nontoxic, environment friendly, and less time consuming. Moreover, hydrothermal synthesis offers several advantages over other synthesis procedures. The work presented here focuses on the synthesis of CQDs from chemical and natural organic precursors in order to exploit their sensing applications in the detection of biomolecules, as peroxidase mimetic catalyst, toxic nitro explosives, and hazardous chemicals.

1.7. Objectives of the study

The objective of the thesis was to develop environmentally safe, straightforward, and cost-effective procedures for synthesis of water-soluble fluorescent CQDs using chemical and natural precursors for potential sensing applications. In order to specifically achieve these aims, the scientific studies undertaken have focused on the following objectives:

- To synthesise mustard carbon quantum dots (M-CQDs) from natural precursors such as mustard seeds via one-pot hydrothermal method.
- To develop M-CQDs showed peroxidase mimetic activity for the detection of hydrogen peroxide and ascorbic acid using colorimetric methods.
- To synthesise doped fluorescent NS-CQDs from chemical precursors as carbon, nitrogen and sulphur sources via one-pot hydrothermal method.
- To assess the biocompatible nature of the synthesized doped NS-CQDs against HeLa cervical cancer cells via cytotoxicity studies using MTT assay.
- To synthesise fluorescent NS-CQDs was exploited as selective Nano-probe for the detection of hazardous explosive picric acid by fluorimetric method.
- To synthesise fluorescent J-CQDs from natural precursors such as Jatropha fruits via one-pot hydrothermal method.

- To evaluate fluorimetric sensor for the detection of chlorpyrifos using as-synthesised fluorescent J-CQDs.
- To characterize these synthesized fluorescent CQDs with Transmission Electron Microscopy (TEM), X-Ray Diffraction Spectroscopy (XRD), Fourier Transform infrared spectroscopy (FTIR), X-Ray Photoelectron Spectroscopy (XPS), UV-visible spectroscopy, Fluorescence spectroscopy, and Time resolved fluorescence life time spectroscopy.